Thermochemistry and the Second Law

More about phase change and chemical reactions

Bond energies and Enthalpy

Heat, Entropy and the Second Law

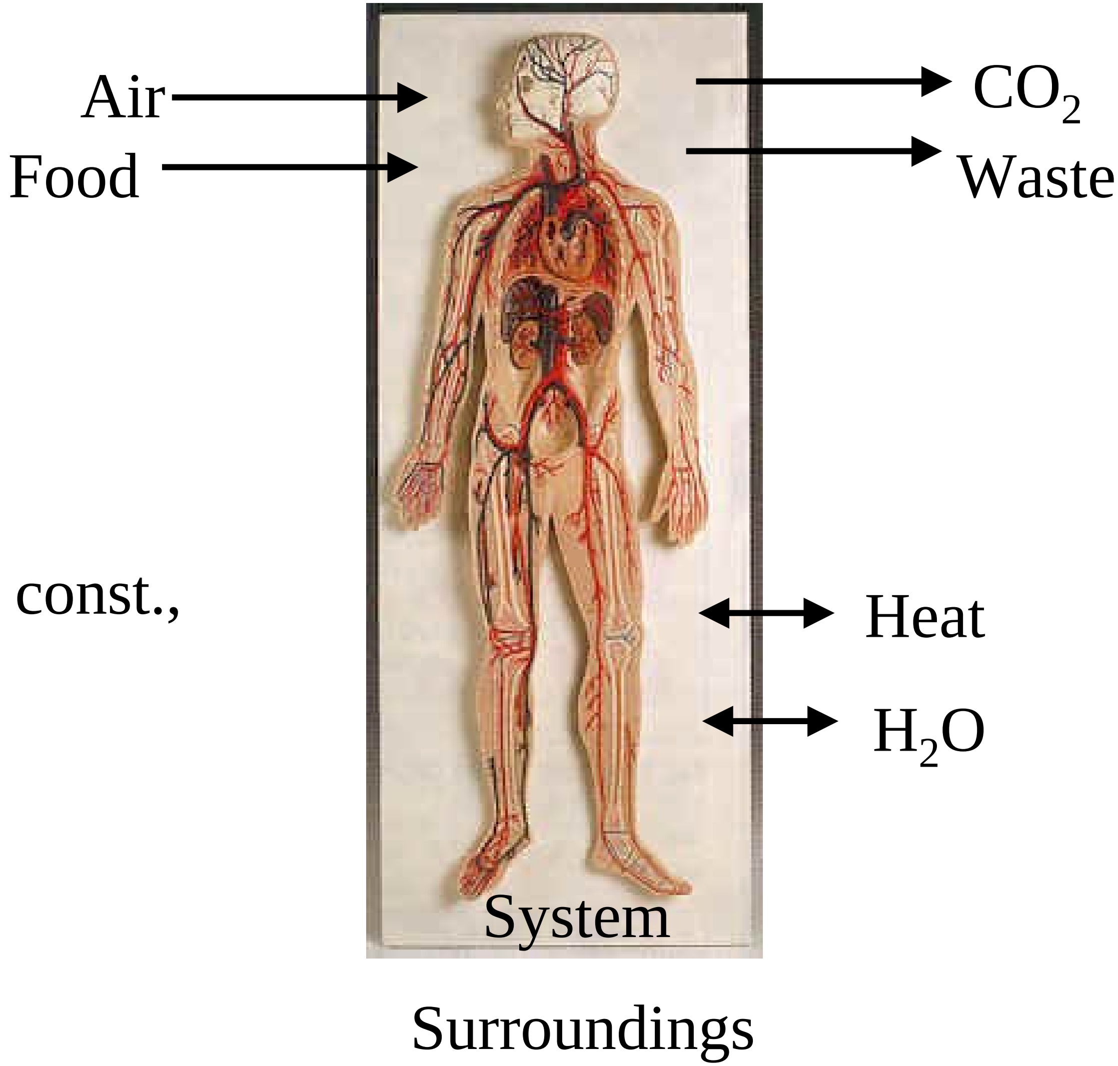
Concept of Complex Conversions

Constraints:

Generally,

T=const., V= const., P= const., m= const.

How do we regulate temperature?



Concept of Complex Conversions

The energy of the system is made up of two pieces:

Kinetic $\propto$ T	Potential
Molecular Vibrations	Molecular rearrangements
Rotations	Aggregation
Translations	Dissolution
	Reactions

On a cold day we lose heat to the surroundings.

Replenished by using food stores: We use up potential energy

On a hot day…..

Perspiration

So during perspiration

$H_2O\ (l) \quad \rightarrow \quad H_2O\ (g)$

Heat transferred to the body goes into causing this transformation

$H_2O\ (l) + \text{heat} \quad \rightarrow \quad H_2O\ (g)$

We can look up the enthalpy for this process at standard pressure

$$\Delta H^\circ_{373} = 2257\ \text{kJ/mol}$$

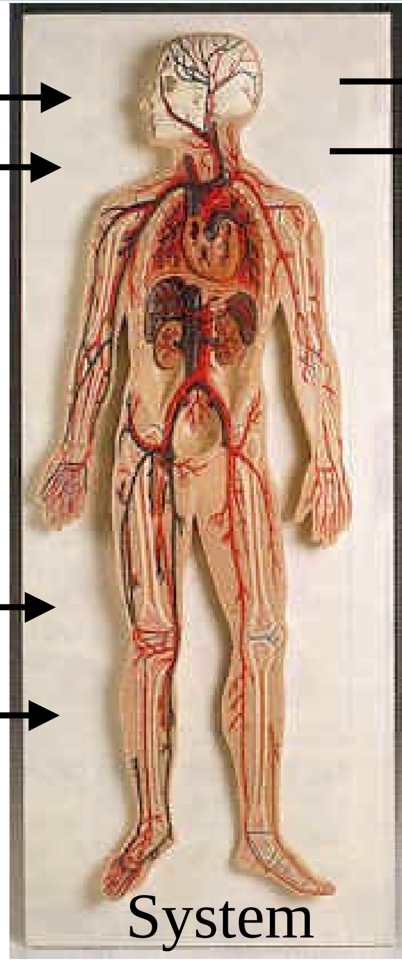
On the other hand the enthalpy of fusion is $\Delta H^\circ_{298} = 333.4$ kJ/mol

Why are these two numbers so different?

Concept of Complex Conversions

Air
Food

CO_2
Waste



Heat
H_2O

Surroundings

Phase Changes:

- Evaporation of sweat
- Condensation of air in the lungs
- Plaque Formation?

Chemical Reactions:

- Metabolism
- Everything else!

Yet another example

This summation property allows us to use information seemingly only tangentially related to our reaction of interest to get to an end point.

We want to know:

$3\ O_2(g,1atm) + 2\ \text{glycine}\ (s) \rightarrow 1\ \text{urea}\ (s) + 3\ CO_2\ (g,\ 1atm) + 3\ H_2O\ (l)$

But we only have:

$3\ O_2(g,1atm) + 2\ \text{glycine}\ (s) \rightarrow 4\ CO_2(g,1atm) + 2\ H_2O\ (l) + 2\ NH_3(g)$

$\Delta H = -1163.5\ kJ/mol$

and

$H_2O\ (l) + \text{urea}\ (s) \rightarrow CO_2\ (g) + 2\ NH_3\ (g)$

$\Delta H = 133\ kJ/mol$

Substracting these last two equations gives the desired result:

$$3\ O_2(g,1atm) + 2\ \text{glycine}\ (s) \rightarrow 4\ CO_2(g,1atm) + 2\ H_2O\ (l) + 2\ \cancel{NH_3}(g)$$

$$-$$

$$H_2O\ (l) + \text{urea}\ (s) \rightarrow CO_2\ (g) + 2\ \cancel{NH_3}\ (g)$$

$$=$$

$$3\ O_2(g,1atm) + 2\ \text{glycine}\ (s) \rightarrow 1\ \text{urea}\ (s) + 3\ CO_2\ (g,\ 1atm) + 3\ H_2O\ (l)$$

$$\Delta H = -1163.5\ \text{kJ/mol} - 133\ \text{kJ/mol} = -1296.8\ \text{kJ/mol}$$

mol= mole of ***reaction!***

Note: To get a biologically reasonable reaction:

$$\text{glycine}(s) + \infty H_2O\ (l) \rightarrow \text{glycine}\ (aq)$$

Temperature Dependence

$$\begin{tikzcd}
A(T2) \arrow[r, "\Delta H(T2)"] \arrow[d, "-C_P^A\,\Delta T"'] & B(T2) \\
A(T1) \arrow[r, "\Delta H(T1)"] & B(T1) \arrow[u, "C_P^B\,\Delta T"']
\end{tikzcd}$$

$$\Delta H(T2) = \Delta H(T1) + \Delta C_P\,\Delta T$$

Phase Changes and Chemical Reactions

Theoretically, what is the difference between a phase change and a chemical reaction?

Both can be written as a conversion of sorts:

H_2O (l) $\rightarrow$ H_2O (g)

2 H_2(g) + O_2(g) $\rightarrow$ 2 H_2O (g)

In both, interactions are formed or broken, heat is released or absorbed, and the enthalpy may be written as:

$$\Delta H = \Sigma n_{pi} H_{pi} - \Sigma n_{ri} H_{ri}$$

Review: Heats of formation

Enthalpy of reactants and products can be calculated from their heats of formation!

$$2\ C(s) + 3\ H_2(g) + 1/2\ O_2\ (g) \rightarrow C_2H_5OH\ (l)$$

Since we can only measure enthalpy changes we have to choose, at some point, and enthalpy of zero.

$\Delta H°_{298}$=0 is the most stable state at standard T and P.

From the table: $\Delta H°_{298,f}$= -276.98 kJ/mol

But this is not a clean reaction in practice. How do we measure it?

Clean Reactions

We sum up the enthalpies of "clean" reactions.

$$C(graphite) + O_2(g) \rightarrow CO_2$$
$$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O$$

$$2\ CO_2(g) + 3\ H_2O(l) \rightarrow C_2H_5OH(l) + 3O_2\ (g)$$

Bond Energies

So we can calculate the heats of formation for many compounds and the reaction enthalpies for many transformations.

From these we can "back-out" average values for how much energy it takes to break a bond.

```
   H H
   |  |
H-C-C-O-H
   |  |
   H  H
```

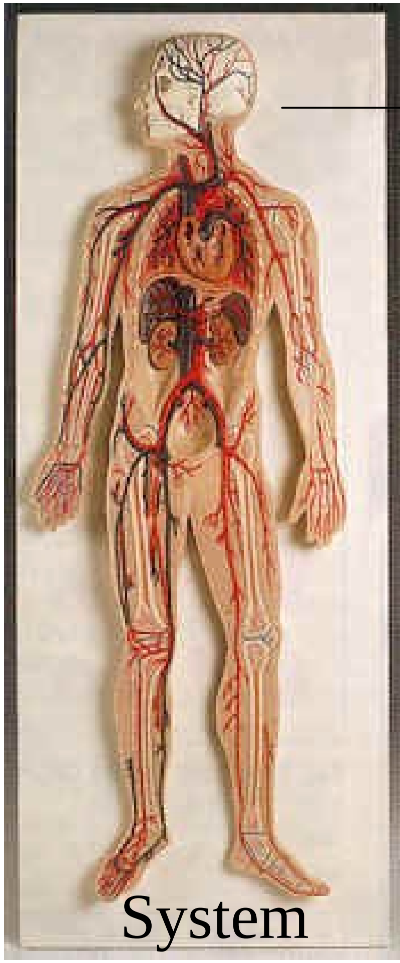
Bond	D(kJ/mol)
C-C	344
C=C	615
C≡C	812
C-H	415
C-N	292
C-O	350
C=0	725
C-S	259
N-H	391
O-O	143
O-H	463
S-H	339
H_2	436
N_2	945.4
O_2	498.3
C(graphite)	716.7

Errors in Bond Energies

$$\mathrm{C(graphite)} + \mathrm{H_2(g)} + \mathrm{O_2(g)} \rightarrow \begin{array}{c}\mathrm{OH}\\ | \\ \mathrm{H\text{-}C{=}O}\end{array}$$

C(graphite)	$\rightarrow$	C(g)	716.7 kJ/mol
$H_2(g)$	$\rightarrow$	2H(g)	436.0 kJ/mol
$O_2(g)$	$\rightarrow$	2O(g)	498.3 kJ/mol
C(g)+ 2H(g) + 2O(g)			1651 kJ/mol
C=O + C-O + C-H + O-H			1953 kJ/mol
Calculated ΔH_f			-302 kJ/mol
Measured ΔH_f			-423.76 kJ/mol

Concept of Complex Conversions



System

Surroundings

100W ~ 9000 kJ/day

1 g protein/carbohydrate=
15kJ= 3.6 Cal

1g fat= 35kJ= 8.4 Cal

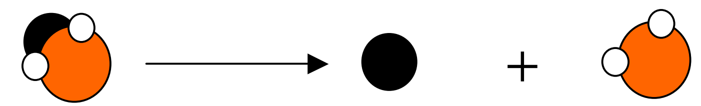
The Matrix

What’s the chemical flaw?

The elements of change

What makes a reaction spontaneous?

Enthalpy → Free energy ← Entropy



$H^\circ_{298}(A)$ $H^\circ_{298}(B)$ $H^\circ_{298}(C)$

$$\Delta H = H(B)+H(C)-H(A)$$

$$\Delta S>0$$

What makes a reaction actually happen?

Molecular Detail, Transport and Kinetics!

The Carnot Cycle

Expansion

State 1 T_{hot} → State 2 T_{hot}

isothermal

$w= -nRT_{hot}\ln(V2/V1)$
$q=-w$

State 2 T_{hot} → State 3 T_{cold}

adiabatic

$q=0$,
$w=-C_V\,\Delta T$

State 3 T_{cold} → State 4 T_{cold}

isothermal

$w= -nRT_{cold}\ln(V4/V3)$
$q=-w$

State 4 T_{cold} → State 1 T_{hot}

adiabatic

$q=0$,
$w=C_V\,\Delta T$

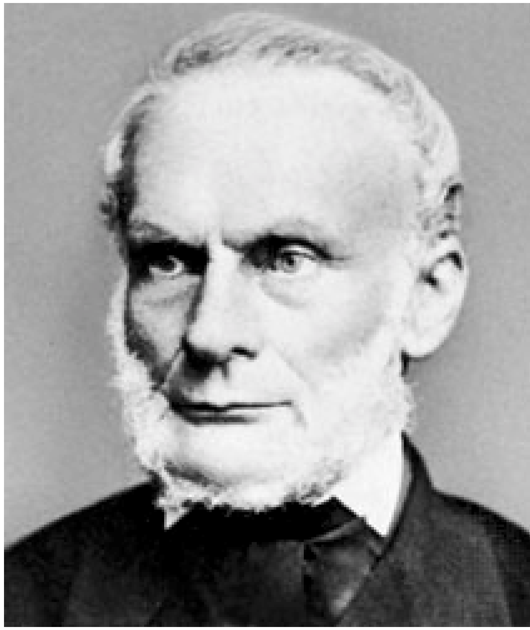
Compression

How much of the heat put in at high temperature can be converted to work?

Can two engines with the same temperature difference drive one another?

What does entropy have to do with it?

Murphy's law and the heat death of the universe!



Clausius

b. Jan. 2, 1822, Prussia
d. Aug. 24, 1888, Bonn

"Heat cannot of itself pass from a colder to a hotter body."

Homework #2

Reading TSW:

chapter 2, pages 41-59

chapter 3, pages 67-80

Problems:

TSW 2.1, 2.6, 2.11, 2.26, 2.34,2.35 (note that 2.26c is redundant)

A humming bird who weighs 20.0 g has a very fast metabolic rate. It expends 4.2 kJ/hour of energy partly as heat and partly as work. How many grams of sugar must it eat per day to provide this energy given the reaction:

$$C_6H_{12}O_6\ (s) + 6\ O_2 \rightarrow 6\ CO_2\ + 6\ H_2O$$

ΔH for this reaction is 16 kJ/mol at 40 °C (hummingbird temp).

(a) Calculate ΔE for this reaction in kJ/gram at 40 °C.

(b) Calculate the number of grams per day a hummingbird must eat.